# THE EFFECT OF SODIUM ON DEPOSITION IN A SIMULATED COMBUSTION GAS TURBINE ENVIRONMENT

Jeffrey S. Ross and Rodney J. Anderson
U.S. Department of Energy
Morgantown Energy Technology Center
Morgantown, West Virginia 26505

Ramamurthy Nagarajan
Department of Mechanical Engineering
West Virginia University
Morgantown, West Virginia 26506

## ABSTRACT

The effect of gas phase alkali concentration on the adhesion properties of micronized coal has been studied using a laboratory-scale entrained reactor capable of accelerating the combustion products of an injected coal-air mixture to the velocities observed in a combustion gas turbine. Alkali metal sulfates are reputed to act as liquid "glue" binders which promote inorganic deposit formation under these conditions. In this study, the concentration of alkali was varied by utilizing a series of naturally occurring coals (Arkwright Pittsburgh bituminous, Spring Creek Montana subbituminous, and North Dakota lignite), and by doping Arkwright coal samples with sodium benzoate. Measured sticking coefficients (i.e., the mass fraction of incident ash which sticks to a deposition target) obtained from this series exhibited trends consistent with the glue hypothesis and with the amount of liquid phase sodium sulfate predicted by equilibrium thermodynamic and vapor deposition rate calculations. Thus, between the melting point and dew point of sodium sulfate, higher sodium concentrations in the coal feed resulted in enhanced sticking. Below the sulfate melting point, the sodium concentration had no effect. These measurements provide a confirmation of the glue-like behavior of sodium sulfate in enhancing deposition rates and represent the first successful probing of the effect of an individual element upon the properties of fly ash originating from natural and chemically doped fuels under gas turbine combustor temperature and velocity conditions.

## INTRODUCTION

One purpose of the U.S. Department of Energy's Fossil Energy Program is the development of technology for use of fossil fuels in the production of energy for domestic consumption. As a part of that program, the Morgantown Energy Technology Center has initiated a program to examine deposition effects in coal-fired heat engines, with the final objective being the development of techniques to mitigate the deposition problem in direct coal-fired gas turbines. This paper reports results from an effort, as a part of that program, to separate the deposition problem from erosion and corrosion and to identify the relationship between deposition and the various chemical constituents in coal.

The use of coal and coal-derived fuels in direct-fired gas turbines provides an attractive alternative to other fuel sources such as petroleum or natural gas. Advantages of coal-based direct-fired turbine systems are the increase in efficiency provided when steam vaporization is removed from the energy production cycle, low capital costs for construction of moderate capacity systems, and a readily available inexpensive fuel. Limitations to the use of coal include dry handling costs and the large fraction of non-combustible material occluded within the coal matrix. Impurities can damage turbine components by a combination of erosion, corrosion, and deposition. These three complications can result in increased maintenance costs and/or losses in cycle efficiency due to either deposit buildup on the airfoils or the imposition of filtration equipment to prevent the problems. The effect of dry handling on the use of coal derives from two sources. First, the technology of dry fuel is considerably different from that of liquid feeding processes. Thus, power plants equipped for diesel or petroleum are not equipped to utilize coal, except perhaps as a coal-water mixture (CWM). However, the formulation of a CWM requires significant grinding of the coal and represents an added expense. Also, the problems of erosion, corrosion, and deposition all require grinding and/or beneficiation of the coal in order to meet gas turbine particulate operating specifications. If these problems can be solved, coal-based plants based on gas turbines can have a distinct competitive price relative to alternatives such as oil, natural gas, or petroleum.

The context of the present study derives from the observation that deposit growth may be promoted by the presence or formation of a liquid layer on the surfaces of ash particles (1,2,3,4). The liquid layer may consist of sodium (or other alkali) sulfate(s) which, due to rapid cooling arising from the expansion out of a gas turbine nozzle, can condense on the surface of an ash particle or on a component surface (rotor or stator blade). The condensation mechanism may be either heterogeneous as observed by Liang, et al. (5), in a recent binary nucleation study or homogeneous as suggested by the calculations of Ahluwalia, et al. (6). Regardless of the mechanism of deposition, experimental determinations of the elemental composition of ash particles have confirmed that surface enrichment does occur on the outer surfaces of fly ash particles (7). In fact, such observations have led to the suggestion that the injection of small particles into combustion turbines could have a mitigating effect on liquid-assisted deposition by acting as sodium gettering sorbents (8).

This set of observations has led to our determination of the "sticking coefficients" of a variety of coals under a wide range of conditions. Portions of this work have appeared as preliminary communications in which the qualitative effects of target temperature, reactor temperature, particle velocity, and coal composition have been discussed (9,10,11). We have now merged our previous deposition results with new observations made on sodium-doped coals and, in an effort to rationalize our observations and predict the sticking behavior of other coals, present those observations within the framework of a preliminary theory of molten glue-assisted deposition (12).

## EXPERIMENTAL

The deposition tests were performed in a laboratory-scale entrained reactor (LETR) which consisted of a mass flow controlled air flow circuit, a particle injection system, a high-temperature furnace, a deposition target assembly, a filtration assembly, and a set of temperature and pressure diagnostics interfaced to a personal computer (Figure 1). The system attempts to simulate deposition processes at the leading edge of a gas turbine. To accomplish this, coal particles are entrained from a fluidized bed feeder and transported into the combustion zone (muffle tube H [Figure 1]) of the LETR. Combustion of the coal leaves the occluded inorganic material entrained as "ash" particles in the hot gas stream. These particles are, in turn, accelerated through a pinhole nozzle located at the end of the muffle tube to velocities in excess of 100 m/s. The degree of acceleration depends upon the temperature of the gas, the pressure drop across the nozzle, and the nozzle diameter. The high velocity particles then impinge upon a platinum target placed normal to the downflow of the gas-particle mixture. Target temperature is measured by radiation pyrometry. The sticking coefficient of the particular sample is obtained as the fraction of ash impinging on the target that actually adheres to the target. A detailed description of the LETR and the typical operating procedure are given below.

### Particle Injection System

The particle injection system consisted of a TSI Model 3400 fluidized-bed aerosol generator (FBAG), a source of dry mass flow controlled compressed air, and a sample splitter, also mass flow controlled, in series with a vacuum pump. Prior to an experiment, the sample compartment of a TSI Model 3400 fluidized-bed aerosol generator was charged with about 10 grams of coal. All coal samples were ground to below -400 mesh (< 40 microns) to facilitate entrainment by the carrier gas. A small motorized conveyor transferred the coal particles into a 1.5-inch diameter bed that was filled with 100 grams of clean copper beads, which served to break up coal agglomerates. A dry air stream was used as both the fluidizing gas and the entrainment gas. The volumetric flow rate of the gas was mass flow controlled at 14 liters per minute, with 80 percent of the flow directed through the bed and the remainder used to purge the particle conveyor. A mass flow controlled aspirator near the entrance of the furnace served to limit the total flow of particle-laden gas to the reactor to below 5.0 liters per minute. The remainder of the gas was exhausted through a filtration system. This throttling was required to hold the nozzle pressure drop within safe limits.

### Furnace Assembly

The furnace was an Astro Industries Model 1000 vertical graphite element tube furnace equipped with a helium purge gas system and an alumina muffle tube assembly. An alumina nozzle (25 mm length, 0.127 mm diameter) was cemented into the muffle tube so that the nozzle exit was 2.5 inches from the exit of the muffle tube. The temperature of the muffle tube was estimated with the aid of two thermocouples, one of which was held in contact with the muffle tube, while the other monitored the temperature adjacent to the heating element. Heating of the tube was accomplished by radiation and conduction through the helium purge gas, which also prevented oxidation of the graphite elements. A set of profiles of the temperature at the center line of the muffle tube (Curves a-c [Figure 2]) obtained with no acceleration nozzle in place were consistent with laminar flow through the furnace.

## Deposition Target Assembly

The platinum target disks (0.25 mm thick, 5 mm diameter) were supported on an Inconel pedestal (Figure 3) bolted to the bottom of the furnace assembly. Pedestal height was adjusted by a series of stainless steel shims in order to position the target at approximately one nozzle diameter (1.27 mm) from the nozzle exit. The pedestal was hollow and contained a quartz lens which focused infrared light emitted from the target onto the entrance of a bifurcated fiber optic bundle. The two legs of the fiber bundle were directed to optical filters with wavelengths of 902.5 nm (14 nm bandwidth) and 1,039.5 nm (19 nm bandwidth), respectively. The transmitted signals were detected by photodiodes, amplified, and output as millivolt signals to an Apple computer. This permitted determination of the target temperature by radiation pyrometry. The targets were weighed to within +/-3 micrograms before and after a deposition run and the deposit weight determined by difference. Deposit weights were typically in the range of 20 to 100 micrograms.

## Filtration Assembly

The arrival rates of ash particles at the target surface were estimated by replacing the target with a filtration assembly fabricated from a combination of a Gelman stainless steel filter holder and a 4-inch porous alumina cylinder. An air flow of 2.0 liters per minute through the porous cylinder provided a radial pressure which prevented deposition of ash vapor and/or particles except on a silver membrane filter (Osmonics, Inc.) held in place by the filter holder. A vacuum pump downstream from the filter was used to balance (via mass flow control) the sampling rate through the filter with the gas input from the furnace exit and the filter inlet. The balance was required in order to prevent escape of particles from the filter and to prevent thermal shock to the muffle tube due to aspiration of room temperature air. In a typical deposition run, three to five filter samples were obtained and used to establish an average ash arrival rate (10 to 80 micrograms per minute, depending on the settings of the particle injection system).

## Preparation of Sodium-Doped Coals

A known amount of sodium benzoate (Fischer Scientific) was dissolved in excess (> 150 mL) of HPLC grade methanol (J. C. Baker) and the clear solution added to a round-bottomed flask containing 10 grams of Arkwright Pittsburgh bituminous coal. The methanol was then removed using a rotary evaporator. The ground glass joints of the evaporator were ungreased to avoid contamination of the coal with silicon. The product consisted of a grayish-black powder with some small whitish lumps of (presumably) pure sodium benzoate occluded within the coal matrix. This material was then ground to pass a 400 mesh screen.

## Typical Deposition Procedure

The coal sample of interest was loaded into the FBAG and the entrainment gas flow and aspiration rates adjusted such that the pressure drop across the acceleration nozzle in the muffle tube was within safe limits and was providing a gas stream of high velocity. During this process, the coal particles were removed from the gas flowing to the reactor by an absolute filter (close Valve 1, open Valves 2 and 5 [Figure 1]) to prevent contamination of the cold furnace. After the muffle tube (heated at a rate of 200°C per hour) and the deposition target reached their appropriate test temperatures, the filter was removed from the flow path (open Valve 1, close Valves 2 and 5 [Figure 1]) and the particle-laden flow was directed into the muffle tube. After collection of several samples, the filtration assembly was removed and the absolute filter reinserted into the particle flow stream. The target assembly was then affixed to the furnace and the target allowed to reach thermal equilibrium in the absence of particles. Blank runs were performed and indicated that deposition ceased when the absolute filter was in the flow path. The absolute filter was then removed from the flow path and the deposition process allowed to proceed for about 1 hour, after which the target was isolated from particles, the target assembly removed, and the target weighed.

### Data Acquisition

Furnace temperature, target temperature, reactor coolant temperature, and nozzle pressure drop measurements were recorded continually during each test by an appropriate interface to a personal computer. For high-speed measurements of the nozzle pressure drop (which determines the nozzle exit particle/gas velocities) and of the target temperature, an IBM PC-AT was employed as a data acquisition device. The IBM interface hardware included a Data Translation DT2805 12 bit A/D board and a DT2807 interface board. Data was acquired by means of a FORTRAN program which employed subroutines from PCLAB and Wiley's FORTRAN Scientific Subroutines, and Fifty More FORTRAN Scientific Subroutines.

## RESULTS AND DISCUSSION

This combined experimental and theoretical report deals only with the effects of deposition in direct-fired coal-burning systems and, therefore, it is appropriate to first outline the justifications for neglecting or removing other effects during the subject experiments (e.g., erosion and corrosion). Also appropriate is a brief discussion of the chosen target design and its relationship to deposition phenomena.

Industrial combustion turbine research has shown that if the gas stream particle size is kept below 10 microns, then deposition and corrosion, not erosion, are the effects responsible for limiting the useful lifetime of a gas turbine (13). This observation was used to decouple erosion from LETR experiments; only micronized coal samples (< 400 mesh) were used. An added benefit of micronized coal is that the particles are easily entrained and when moving through the apparatus, they follow the flow paths of the gas (i.e., they have a negligible inertial slip velocity). This helps to eliminate deposition of slag within the reactor which could develop in a drop tube by overloading of the combustion zone. Some of the detrimental effects of slagging in a test reactor are changing combustion heat transfer properties, a buildup of liquid/glass phase species of unknown vapor pressure that could contaminate future samples, and variation within sample runs of the equilibrium vapor pressures of slag components. By employing the entrainment principle, the combustion zone loading is sufficiently low to avoid slagging.

The decoupling of corrosion from LETR experiments was accomplished by fabricating the targets from platinum metal. This is justified by the inertness of platinum toward oxidation, poor affinity for adsorption of gases such as carbon monoxide and carbon dioxide, and resistance to attack by hot corrosive liquids (14,15,16). An important qualification which has not been addressed is the utility of deposition data in absence of the competing effects of erosion and corrosion.

Conversely, after combustion of the coal particles, it is desirable to force as much of the ash as possible to impact upon the target. The use of a target placed normal to the gas stream at the nozzle exit satisfies this condition if the target diameter is much larger than the nozzle diameter and if the target is located less than five nozzle diameters from the nozzle exit (17). This design was employed in the LETR and imposed the requirement of zero velocity (both particle and gas) at the target surface. The overall result is that a stagnation point has been created at the intersection of the target and the expanding gas-particle jet. The significance of this is that particle arrival rates and vapor deposition rates are at or near their maximum values under stagnation conditions which should result in the observation of the maximum effect of an additive upon coal ash deposition properties. Finally, the leading edge of a gas turbine blade also has a stagnation line configuration.

Deposition data was obtained for the following coals: Arkwright Pittsburgh bituminous (APB), Spring Creek Montana subbituminous (SCMS), AMAX-II (cleaned) Kentucky bituminous (KB), North Dakota lignite (NDL), and acid-washed North Dakota lignite (AWL). The ultimate analyses for these coals are presented in Table 1. Figure 4 shows a plot of the "sticking coefficient" (mass fraction of material adhering to the target) obtained for these coals at a variety of target temperatures.† These data are reproducible to within about ± 20 percent. Although NDL has the highest ash content and the highest sticking coefficient, the correspondence between ash content and sticking coefficient does not continue for the other coals. Similarly, although increased sodium content may increase the fouling tendencies of coal, a simple (i.e., linear) correspondence between sodium and sticking coefficient does not appear to be operative here. Furthermore, the ordering of the sticking coefficients is not explained by simple parametric indices such as the fouling index (10,18). Thus, although the extreme cases agree with predictions based on coal ash content, alkali level, or fouling index, a more detailed description of coal ash sticking must be employed in any rational analysis of ash deposition.

The approach offered here is to use the ash analysis as an input for chemical equilibrium thermodynamic calculations to determine the amount of liquid glue likely to be present in the deposit at a given deposition temperature. The quantity of liquid phase was, in turn, used as input for the sticking code (vide infra) and directly compared to the observed sticking coefficients (Figure 4). The first step in our predictive procedure is calculation of combustion deposit compositions based on the premise that the condensed solution phases indicated by an equilibrium thermodynamic analysis are the ones likely to appear on the target surface. The NASA CEC free-energy minimization computer program (19) is widely used toward this end in spite of several numerical difficulties associated with its newly acquired ideal solution capability; these are usually singular matrices and convergence problems

† There is no provision in the LETR to vary the target temperature independently of the combustion gas temperature; this makes it difficult to decouple the effects of the two temperatures on the sticking coefficient.

are encountered when condensed phases are added. Significant improvements (i.e., the addition of a phase rule check) have been incorporated in the PACKAGE code (20) which is, thus, essentially a more robust version of the CEC-solution code. Due to its demonstrable efficiency in analyzing the complex phase equilibria in coal conversion gas streams and cleanup devices, the PACKAGE program has been used to perform the equilibrium/thermodynamic computations presented here.

Having obtained the condensed liquid phase fraction and composition by exercising the PACKAGE code at the pressure, surface temperatures, and feed compositions of interest, the steady-state sticking coefficient, s, of impacting fly ash particles is evaluated in the presence of the deposited liquid glue. This is done by means of a mechanistic theory of deposition (12) which incorporates impaction/diffusion interactions neglected in previous work. Briefly, the principles underlying this theory of "self-regulated" liquid-enhanced capture of supermicron ash may be stated as follows. The inertial impaction deposition rate will depend linearly on s, but s itself will depend on the inventory (and physical properties) of "glue" available to each particle on the deposit surface layer. Therefore, the steady-state values of s and particle deposition rate must be obtained by solving a coupled nonlinear equation. This fundamental concept is discussed in more detail by Rosner and Nagarajan (12) and Ross, et al. (21).

In Figure 5, the PACKAGE-generated liquid-condensate mole fraction is plotted as a function of surface temperature for the four coals. The glue-liquid solution (assumed to be ideal) is comprised principally of alumino-silicates, silicates, oxides, and sulfates of calcium, potassium, sodium, aluminum, silicon, and titanium. Solid phases predicted to separate out include $Al_2TiO_5$, $Al_2SiO_5$, $CaAl_2Si_2O_8$, $CaSO_4$, $Fe_2O_3$, $K_2SO_4$, and $SiO_2$; these are relatively benign with respect to fouling and corrosion, although they could contribute to the erosion of surface material if they were encapsulated in particles larger than about 10 μm diameter. The plotted results show that a minimum fraction of feed material condenses as liquid for KB, while NDL experiences maximum liquid inundation. However, the Arkwright Pittsburgh and Montana subbituminous coals are inverted with respect to Figure 4. Thus, as with ash content, alkali level, and fouling index, the fraction of condensing material in the combustion product stream gives a reasonable qualitative indication of the sticking propensity of the coal-ash but does not correlate exactly with the sticking coefficient, s. This demonstrates the inadequacy of a strictly thermodynamic analysis to predict the sticking coefficient and again hints at some unknown but vital piece of information required to provide an accurate gauge of deposition behavior. To address this problem, the thermodynamic analyses have been combined with the effects of mass transfer between the gas mainstream and the deposition surface, with the assumption that s depends primarily upon the relative arrival rates of ash particles and glue-liquid to the surface.

Using the thermodynamic data to provide the total condensed phase fraction at a given temperature and providing that data to a modified version of the self-regulated sticking computer code (based on the work of Rosner and Nagarajan [12]), calculated sticking coefficients can be obtained for each of the tested coals (Figure 6). Now the predicted ordering of coals with respect to their sticky nature is in line with experimental observation (i.e, NDL >

SCMS > APB > KB).† There is even good quantitative agreement in certain ranges of surface temperature. Discrepancies between the measured temperature dependence of $\underline{s}$ and the prediction may be accounted for by uncertainties in the experimental data collection procedure or limitations in the accuracy of the admittedly preliminary model for sticking or, most likely, both. For instance, the theory does not model the process of ash softening due to high-energy impact (12) in sufficient detail. Improvements to the present theoretical model will be made as fresh data or insight into the physical processes become available.

Another facet of the LETR deposition tests was to study the effectiveness of metallic additives in mitigating deposition-related problems as well as to identify troublesome coal constituents that need to be selectively removed. There are a few precedents reported in literature for our additive strategy. Nagarajan (22) has investigated the use of trace additives to minimize turbine blade "hot corrosion" due to molten alkali sulfate condensation from jet fuel combustion gases. Rathnamma and Nagarajan (23) have studied high-temperature corrosion control by metal additions to vanadium-contaminated fossil fuels. A recent study conducted by Battelle Columbus Laboratories evaluated the use of chemical additives to reduce gas-side fouling and corrosion in oil- and coal-fired systems (24). Attempts have been made to counteract high-temperature fouling with $CaCO_3$ and with boron-, manganese-, and magnesium-based additives. The Saskatchewan Power Corporation has used limestone to combat ash fouling in boilers fired with lignite (24). Austin (25) has examined the effect of sodium on the strength of sintered ash mixtures. The effects of added alumina and emathalite particles were investigated by Shannon (26) in an effort to reduce alkali concentration by gettering sodium in the combustion process.

However, even when such tactics have proved to be successful, the reasons for the success have not been clearly understood, particularly in coal combustion applications. In order to address this deficiency in our appreciation of the roles played by the individual additives, our research does not merely acquire empirical information regarding the "best" additive, but attempts to gain insight into what makes the "best" additive so effective.

The first round of deposition tests in the LETR were conducted with sodium benzoate as the metal-containing additive. Upon addition of a 30-fold excess of sodium to a sample of APB coal, the sticking coefficient at 1,107 K was raised from about 0.15 to about 0.6, a four-fold magnification. This is consistent with the formation of a larger condensed phase fraction following the addition of a large excess of sodium (Figure 9). Sticking coefficients obtained for lower target temperatures (< 1,000 K) showed no change upon addition of the sodium, which is expected because the liquid phase fraction is not sensitive to sodium level as the temperature decreases significantly below the melting point of sodium sulfate (1,157 K). Future experiments will utilize dopants containing aluminum, magnesium, calcium, and other metals.

---

† The lower ash content of the Spring Creek coal relative to the Arkwright coal implies a larger inventory of glue available per impacting particle and, hence, enhanced sticking coefficients.

An equilibrium thermodynamic analysis of the effect of these additives on condensed liquid formation during the combustion of the APB coal in the LETR has been carried out and the results are displayed in Figures 8 and 9. In these figures, the mole fraction of the molten solution condensate in the combustion product mixture is plotted against additive concentration, the axes being nondimensionalized with respect to corresponding reference Arkwright coal values. From Figure 8, it appears that iron, silicon, calcium, and aluminum are all effective suppressants of glue-liquid formation, with aluminum being the most effective of these. Figure 9 indicates that potassium, sulfur, and titanium are bad additives (i.e., adulterants that should be removed from the coal to reduce its fouling tendency). Sodium and magnesium additions do not result in monotonic trends; 10 times as much sodium in the seeded coal as in the reference coal results in a minimum solution phase fraction, and about 10 times as much magnesium results in maximum. Since, on the basis of the ash deposition theory (12), these phase fractions correlate fairly well with predicted sticking coefficients, an optimum level of each additive that minimizes sticking may be determined on the basis of these plots. However, the added mass loading introduced may increase erosion of machine components even though fouling is alleviated. These considerations, while of secondary importance to this paper, should certainly be included in a more ambitious life prediction venture.

The influence of sodium and aluminum additives on the predicted sticking coefficient at a LETR target temperature of 1,107 K is displayed in Figure 7. With the addition of sodium beyond 10 times its level in the reference Arkwright coal, $\underline{s}$ begins to increase until it reaches a value of about 0.6 at 30 times the reference value of sodium concentration which is in reasonably good quantitative agreement with the experimentally measured sticking coefficient under these conditions. In the aluminum added case, $\underline{s}$ drops to about a third of its value of 0.6 (corresponding to combustion of sodium-enriched coal) with the addition of only about five times as much aluminum as is present in the reference Arkwright coal and remains nearly constant with further increases in the aluminum concentration. The predictions in Figure 7 also suggest the interesting possibility of decreased $\underline{s}$ upon addition of smaller quantities of sodium; a fact which no doubt contributed to the lack of correlation between alkali level and sticking coefficient. These trends will be explored as testing of sodium- and aluminum-doped coals continues. A confirmation, based on such comparisons, of the accuracy of our theory in predicting sticking behavior of coals will imply the availability of a powerful predictive tool that will enable us to evaluate different coals with respect to their fouling characteristics and aid in the development of suitable seeding/cleanup techniques to minimize ash deposition.

To assist in acquisition of the sticking data, a new deposition test facility has been fabricated. It is performance rated at 12 atmospheres as opposed to the previously available atmospheric pressure LETR unit and contains three sets of optical access ports which permit the use of non-intrusive optical diagnostic equipment. The combustion/deposition entrained reactor (CDER) has a higher throughput, a wider range of accessible velocities and temperatures, a temperature-controlled target assembly, and an extensive set of automated control features. In addition, the target assembly may be modified to examine impaction geometries other than 90° and thereby extend our studies beyond the stagnation point to model deposition on the pressure and vacuum sides of a gas turbine blade. Some of the code modifications under way include an improved description of deposit thermal conductivity (21), incorporation of deposit shape effects and differential sticking coefficients (obtained from high-speed photography of growing deposits), addition of a subroutine to allow glue uptake by particles during their transit across the boundary layer (this may be studied experimentally by methods similar to those of Liang [5]), consideration of simultaneous deposit erosion (i.e., negative instantaneous sticking coefficients), and incorporation of phase change processes and particle-glue diffusion within already formed deposits (possibly accessible by in situ specular reflectance FTIR).

## CONCLUSIONS

Predictions of ash fouling behavior have previously been made based on a variety of empirical or thermodynamic factors. Unfortunately, neither the empirical parameters (i.e., sodium level, fouling index) nor the thermodynamics-based liquid phase fraction provided an adequate prediction of the sticking behavior of a given coal. However, by a combination of thermodynamic analysis via the PACKAGE code to obtain liquid phase fractions and the application of that data within the context of the self-regulated sticking concept (12), a fairly good comparison was obtained between predicted sticking values and experimental results. This was especially encouraging because the self-regulation concept is still in its developmental stages.

The overall objective of this research has been to suggest methods of mitigating the deposition process in direct coal-fired gas turbines and, thus, relieve the economic burdens of maintenance and aerodynamic efficiency loss. The good agreement between the simple equilibrium/mass transfer model and the sticking coefficients obtained in the LETR represents a first step toward that objective. Thus, given the ultimate analysis of a particular lot of coal, the propensity of that coal to form deposits in a boiler or gas turbine could be determined. In addition, specific coal cleaning procedures or coal additives could be recommended to mitigate the formation of deposits. A combined experimental and theoretical program has been initiated that extends the work presented here to provide a data base of standard coal, coal additive, and pure mineral sticking coefficients. In the course of these tests, the sticking model will be updated to better reflect conditions within actual gas turbines. Future manuscripts will provide detailed comparisons between the operational characteristics of real-life gas turbines and the deposition and combustion environments in the LETR and the CDER, and the relationships between sticking coefficients, turbine fouling rates, and actual as well as simulated turbine deposit compositions.

## ACKNOWLEDGMENTS

This work was funded by the U.S. Department of Energy's Fossil Energy Advanced Research and Technology Development Program. Jeffrey S. Ross acknowledges funding through the Oak Ridge Associated Universities Postdoctoral Training Program. The authors appreciate the assistance of Dale W. Wilson, Jr. in construction of the apparatus, David R. Goff in the design of the two-color optical pyrometer, and Cindy J. Romanowski for the collection of some of the experimental data.

## DISCLAIMER

The use of trade names by the authors of this paper does not imply the endorsement of any product, apparatus of configuration by the authors, the U.S. Department of Energy, or by Oak Ridge Associated Universities. Such references are made only for the purpose of clarity.

## REFERENCES


1. Cross, N.L., and R.G. Picknett, "Particle Adhesion in the Presence of a Liquid Film," The Mechanism of Corrosion by Fuel Impurities, H.R. Johnson and D.J. Littler, eds., Butterworths, London, pp. 383-390 (1963).

2. Wibberley, L.J., and T.F. Wall, "Alkali-Ash Reactions and Deposit Formation in Pulverized Coal-Fired Boilers: The Thermodynamic Aspects Involving Silica, Sodium, Sulphur, and Chlorine," Fuel, 61, 87-92 (1982).

3. Wibberley, L.J., and T.F. Wall, "Alkali-Ash Reactions and Deposit Formation in Pulverized Coal-Fired Boilers: Experimental Aspects of Sodium Silicate Formation and the Formation of Deposits," Fuel, 61, 93-99 (1982).

4. Wibberley, L.J., and T.F. Wall, "Deposit Formation and Sticky Particles from Alkali-Ash Reactions," Fouling and Slagging Resulting from Impurities in Combustion Gases, R.W. Breyers, ed., Engineering Foundation, New York, New York, pp. 493-513 (1983).

5. Liang, B., A. Gomez, J. Castillo, and D.E. Rosner, "Experimental Studies of Nucleation Phenomena within Thermal Boundary Layers -- Influence on Chemical Vapor Deposition Rate Processes," submitted to AIChE Journal.

6. Aluwalia, R., K. Im, C.F. Chuang, and H.K. Geyer, "Evolution and Deposition of Ash Particles in Coal-Fired Gas Turbines," Proceedings of the First Annual Heat Engines Contractors Meeting, May 1-3, 1986, pp. 317-325, DOE/METC/84-31(CONF-8405138--)(DE85001953).

7. Raask, E., "Creation, Coalescence, and Capture of Mineral Species in Coal Flames," J. Institute of Energy, 231-239 (1984).

8. Scandrett, L.A., and R. Clift, "The Thermodynamics of Alkali Removal from Coal-Derived Gases," Journal of the Institute of Energy, 391 (1984).

9. Anderson, R.J., C.J. Romanowski, and J.E. France, "The Adherence of Ash Particles from the Combustion of Micronized Coal," Research Report, DOE/METC-85/2007 (DE 85008600), October 1984.

10. Anderson, R.J., C.J. Romanowski, R.E. Conn, and R.A. Dennis, "Deposition Effects in the Combustion of Coal-Derived Fuels," Proceedings of the Advanced Research and Technology Development (ARTD) Direct Utilization Contractors Review Meeting, 252-264 (August 1985). DOE/METC-85/6027 (DE85013718).

11. Anderson, R.J., S.D. Woodruff, R.A. Dennis, and J.S. Ross, "Deposition Effects in the Pressurized Combustion of Coal-Derived Fuels," Proceedings of the Advanced Research and Technology Development (ARTD) Direct Utilization Contractors Review Meeting, September 1986, in Press.

12. Rosner, D.E., and R. Nagaranjan, "Toward a Mechanistic Theory of Deposit Growth from Ash-Laden Flowing Combustion Gases: 1. Self-Regulated Sticking of Impacting Particles in the Presence of Vapor- or Submicron Mist Glue," to be presented at the AIChE-ASME-ANS National Heat Transfer Conference, Pittsburgh, Pennsylvania, August 9-12, 1987.

13. Hoy, H.R., A.G. Roberts, and J. Stringer, "Combined-Cycle Power Plant Via Pressurized Fluidized-Bed Combustion," Proceedings of the Second Conference on Advance Materials for Alternative Fuel Capable Heat Engines," U.S. Department of Energy and Advance Fuel Research Institute, 2-115 (1985).

14. Satterfield, C.N., "Heterogeneous Catalysis in Practice," McGraw-Hill, New York (1980).

15. Klabunde, K.J., "The Chemistry of Free Atoms and Molecules," Academic Press, New York (1980).

16. Speight, J.G., "The Chemistry and Technology of Coal," Marcel Dekker, New York (1983).

17. Marple, V.A., and K. Willeke, "Impactor Design," Atmospheric Environment, 10, 891-896 (1976).

18. Ghosh, S.K., "Understanding Thermal Coal Ash Behavior," Mining Engineering, 158-162 (1986).

19. Gordon, S., and B.J. McBride, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations," NASA Sp-273, Interim Revision, March 1976.

20. Yousefian, V., M.H. Weinberg, and R. Haimes, "PACKAGE (Plasma Analysis, Chemical Kinetics, and Generator Efficiency): A Computer Program for the Calculation of Partial Chemical Equilibrium/Partial Chemical Rate Controlled Composition of Multiphase Mixtures Under One-Dimensional Steady Flow," Aerodyne Research, Inc., Report No. ARI-RR-177 (1980).

21. Ross, J.S., M. Ramezan, R.J. Anderson, and R. Nagarajan, "Prediction and In Situ Measurement of the Thermal Conductivity of Multiphase Fouling Deposits Formed in Direct Coal-Fired Combustors," to be presented at the ASME 1987 Winter Annual Meeting Session on Measurements in Combustion Equipment, Boston, Massachusetts, December 13-18 (1987).

22. Nagarajan, R., "Theory of Multicomponent Chemical Vapor Deposition Boundary Layers and Their Coupled Deposits," Dissertation Thesis, Department of Chemical Engineering, Yale University, May 1986.

23. Rathnamma, D.V., and R. Nagarajan, "High-Temperature Hot Corrosion Control by Fuel Additives," to be presented at the Tenth International Conference on Metallic Corrosion, Madras, India, November 7-11, 1987.

24. Marner, W.J., "Gas-Side Fouling," Mechanical Engineering, pp. 70-77, March 1986.

25. Tangsathitkulchai, M., and L.G. Austin, "Studies of Sintering of Coal and Ash Relevant to Pulverized Coal Utility Boilers," Fuel, 64, 86-92 (1985).

26. Shannon, S., MS Thesis, University of Pittsburgh, 1986.

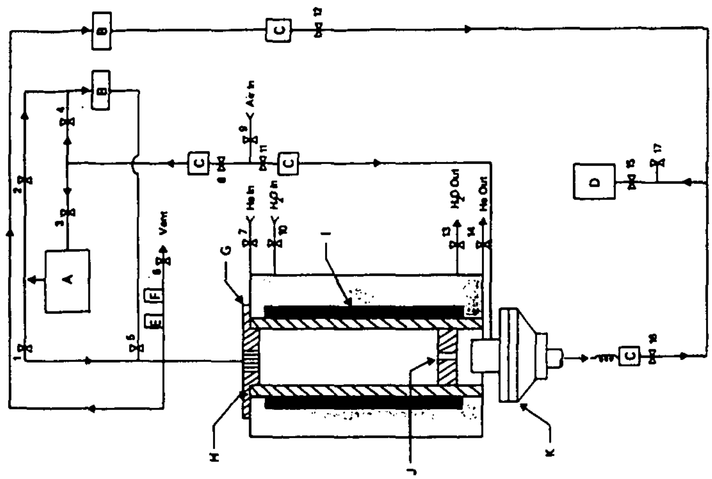

Figure 1. Laboratory Entrained Test Reactor (LETR) Schematic Drawing: A, Fluidized-bed aerosol generator; B, Absolute filters; C, Mass flow controllers; D, Vacuum pump; E, Pressure relief valve; F, Pressure transducer; G, Preheater with flow straightener; H, Alumina muffle tube; I, Graphite heating element; J, Acceleration nozzle; K, Filter holder.

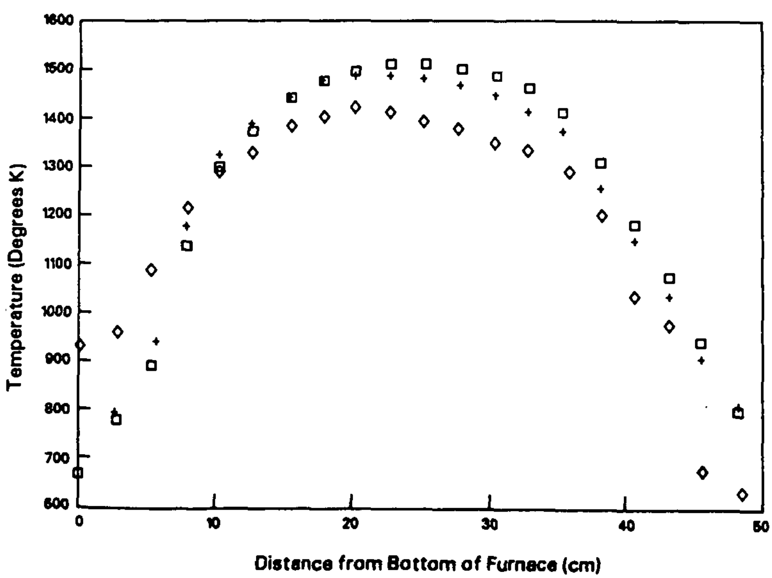


Figure 2. Temperature Profile in the LETR Without a Nozzle: □, 42 m Volts and 0.3 lpm; +, 42 m Volts and 1.0 lpm; ♦, 42 m Volts; and 3.0 lpm.

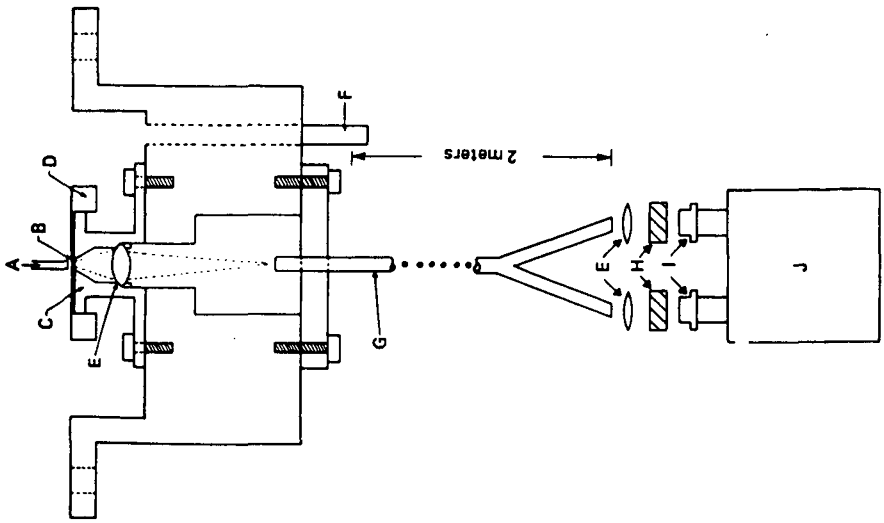


Figure 3. Target Assembly with Fiber Optic Pyrometer: A, Nozzle; B, Target; C, Target Pedestal; D, Target Retaining Ring; E, Lens; F, Exhaust; G, Fiber Optic; H, Optical Filter; I, Detector; J, Signal Amplifier, Electronics and Computer Interface.

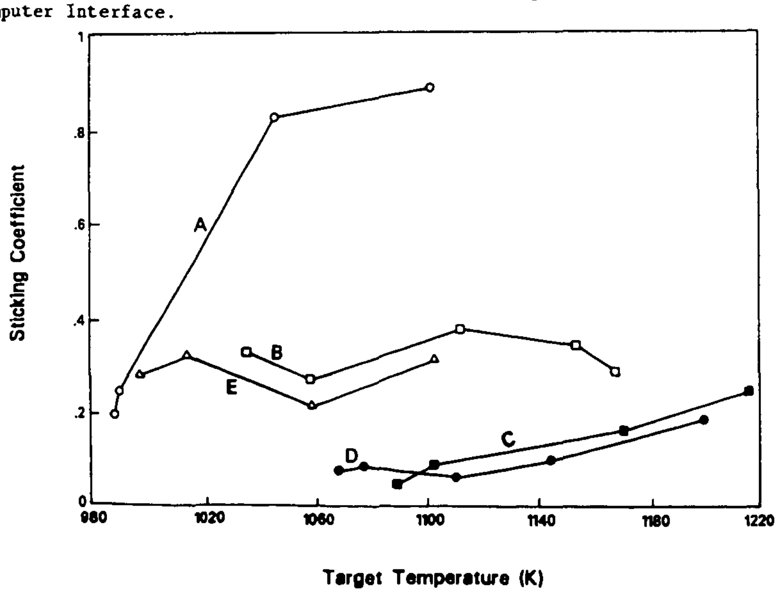


Figure 4. Measured Values of Sticking Coefficient Versus Target Temperature for Tested Coals: A, North Dakota Lignite; B, Spring Creek Montana Subbituminous; C, Arkwright Pittsburgh Bituminous; D, Kentucky (Cleaned AMAX-2) Bituminous; E, Acid Washed Lignite.

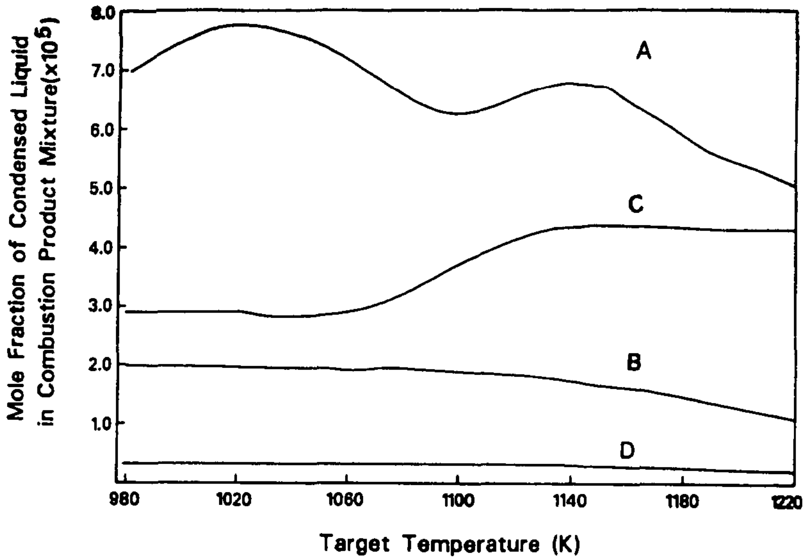


Figure 5. Predicted Values of Condensed Glue Fraction Versus Target Temperature for Tested Coals: A, North Dakota Lignite; B, Spring Creek Montana Subbituminous; C, Arkwright Pittsburgh Bituminous; D, Kentucky (Cleaned AMAX-2) Bituminous.

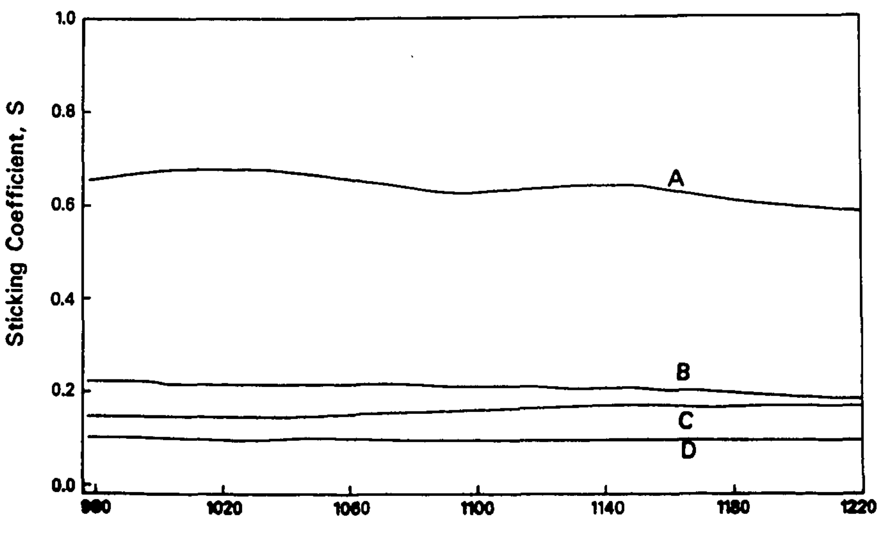


Figure 6. Predicted Values of Sticking Coefficient Versus Target Temperature for Tested Coals: A, North Dakota Lignite; B, Spring Creek Montana Subbituminous; C, Arkwright Pittsburgh Bituminous; D, Kentucky (Cleaned AMAX-2) Bituminous.

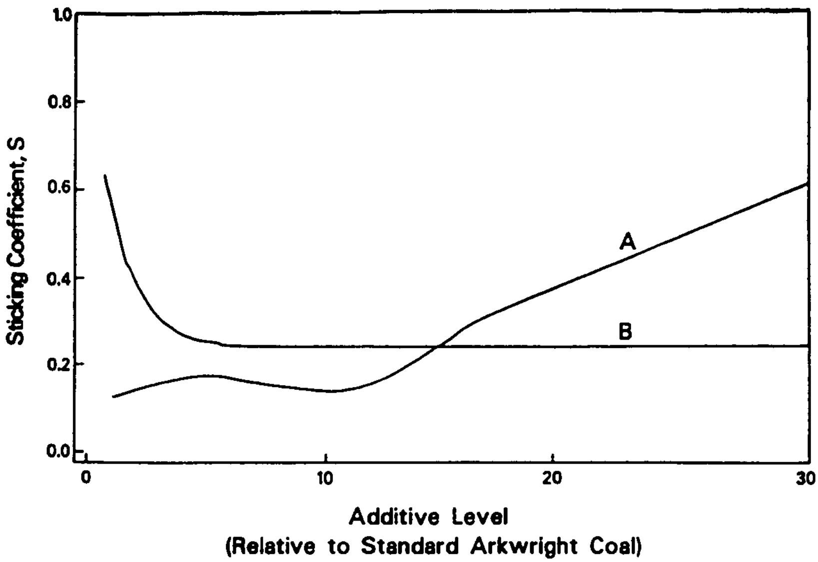


Figure 7. Predicted Effect of Additives on Impacting Ash Particle Sticking Characteristics in the LETR. Target Surface Temperature = 1107 K. A, Sodium; B, Aluminum.

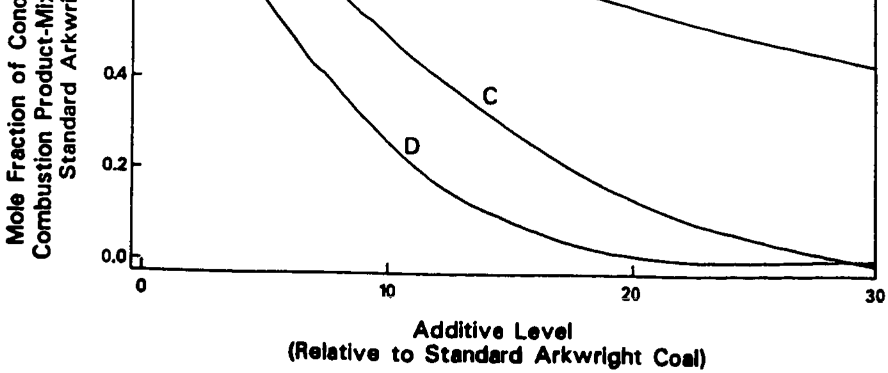


Figure 8. Predicted Effect of Additives in Supressing Condensation of Liquid Glue on the Target Surface in the LETR. Target Surface Temperature = 1107 K. A, Iron; B, Silicon; C, Calcium; D, Aluminum.

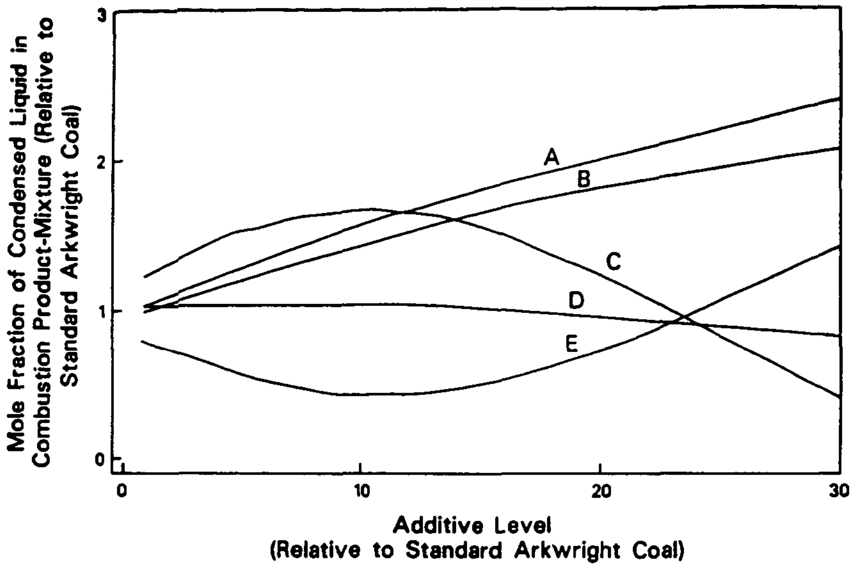


Figure 9. Predicted Effect of Additives on Condensation by Liquid Glue on Target Surfaces in the LETR. Surface Temperature = 1107 K. A, Potassium; B, Titanium; C, Magnesium; D, Sulfur; E, Sodium.

TABLE 1

Ash Composition of Coals Tested in LETR

| COAL / RANK | Arkwright Pittsburgh Bituminous | Kentucky (Cleaned) Bituminous | Spring Cr. Montana Subbituminous | North Dakota Lignite | North Dakota (Acid Washed) Lignite |
|---|---|---|---|---|---|
| % ASTM ash | 6.93 | 0.68 | 2.30 | 20.45 | 16.05 |
| Ash Comp. (Wt%) | | | | | |
| $SiO_2$ | 48.09 | 25.48 | 18.6 | 20.08 | * |
| $Al_2O_3$ | 25.07 | 15.92 | 13.5 | 11.19 | * |
| $Fe_2O_3$ | 10.95 | 32.35 | 4.7 | 13.19 | * |
| $TiO_2$ | 1.27 | 7.77 | 1.3 | 0.48 | * |
| $P_2O_5$ | 0.18 | 0.48 | 0.4 | 0.28 | * |
| CaO | 5.78 | 1.32 | 26.5 | 22.85 | * |
| MgO | 1.25 | 0.62 | 6.5 | 6.68 | * |
| $K_2O$ | 1,16 | 0.30 | 0.1 | 0.32 | * |
| $Na_2O$ | 0.90 | 9.53 | 13.1 | 8.26 | * |
| $SO_3$ | 5.34 | 6.22 | 15.4 | 16.07 | * |

* An insufficient quantity of coal ash was available for quantitative analysis.